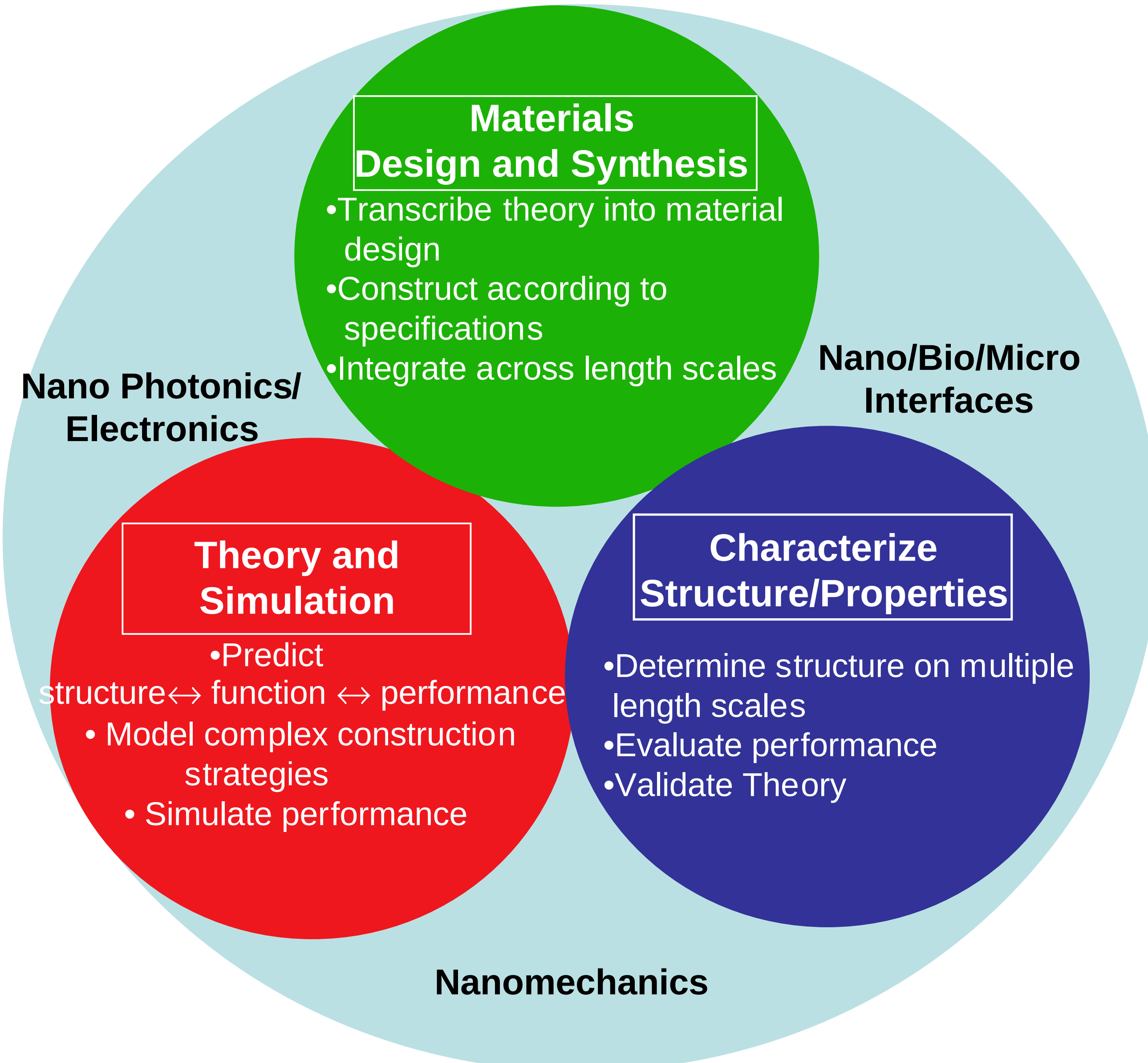
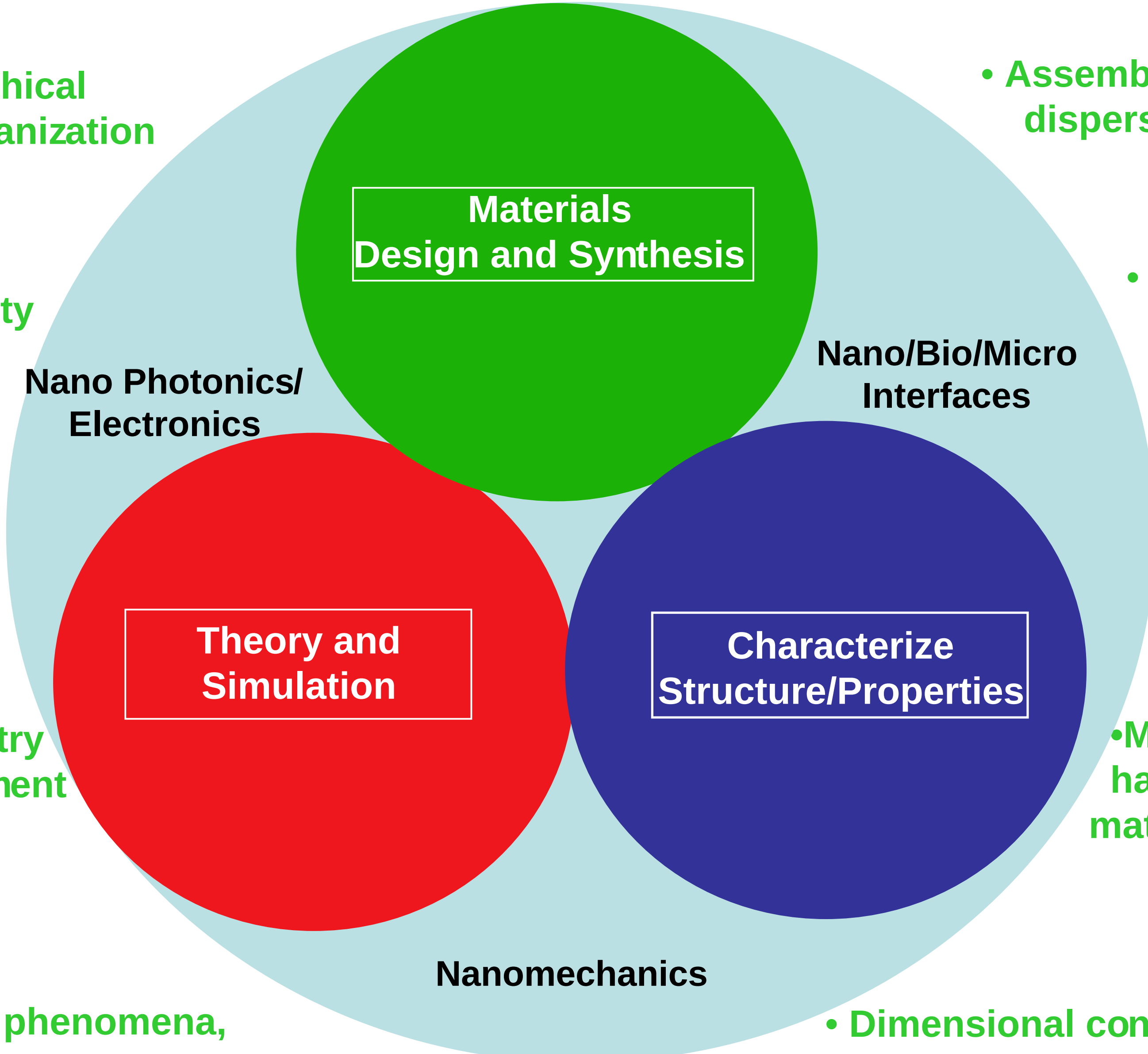
Complex Functional Materials



Complex Functional Materials

Synergistic and often emergent properties arise due to:



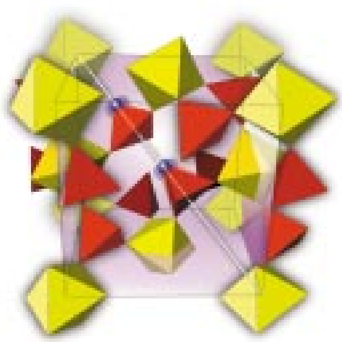
- Hierarchical organization
- Switchability
- Asymmetry alignment
- Interfacial phenomena, curvature
- Gradients
- Assemblies, arrays, dispersion
- Unconstrained lattices
- Mixtures of hybrid hard and soft materials
- Dimensional confinement in 1,2, or 3-D (dots, tubes, layers)

CFN Thrust Will Explore Nano-Structured Materials Designed and Synthesized on Different Length Scales

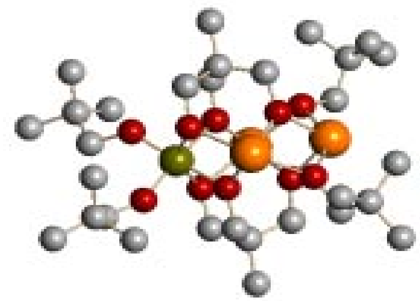
Nanocells

Many materials with unique functionality have complex, nm-scale crystal structures

Novel precursor chemistries enable complex materials synthesis

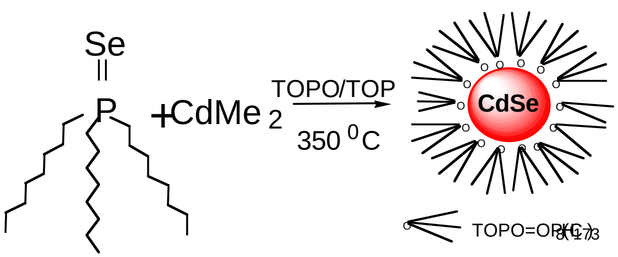


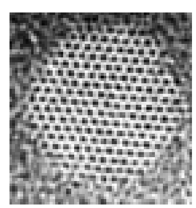
Nanometer Unit Cell-
ZrW_2O_8
↓
Underconstrained lattice
↓
Negative Thermal Expansion



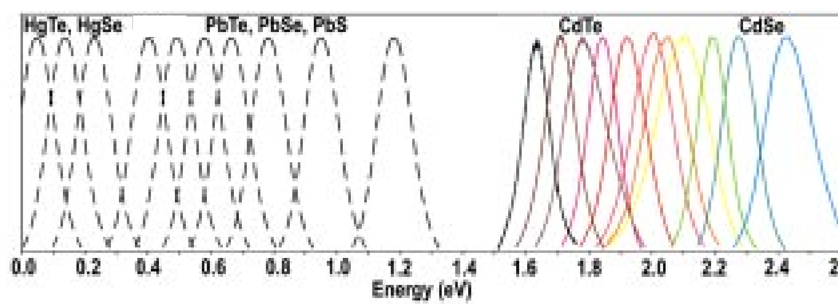
(m-THME)Sn_3Ti(m-ONep)$_2$(ONep)$_2$

- Size, shape and composition control for tuning electronic and optical properties of quantum dot building blocks:



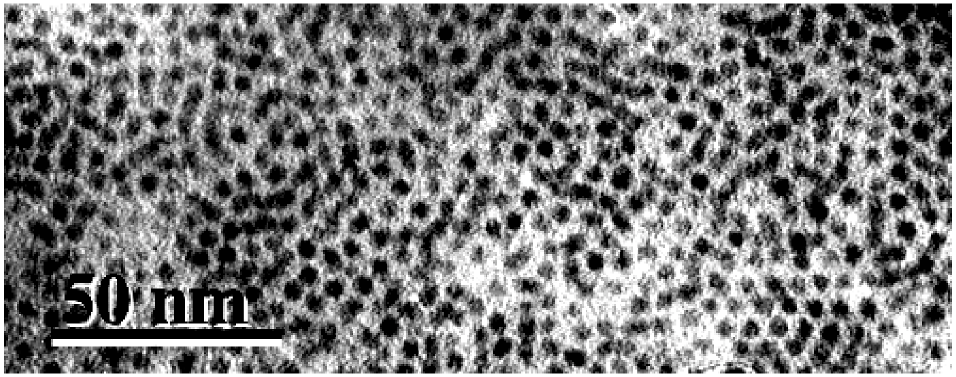


R = 10—70 Å, δR/R= 4—7%



Tunable emission via size and composition control

Quantum Dot Molecules and Solids Represent New Types of Artificial Solids

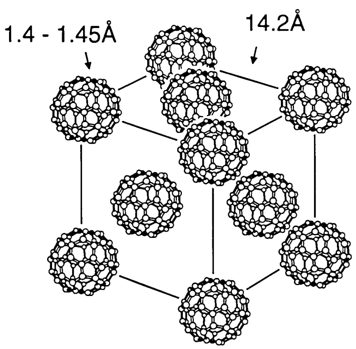


R = 12 Å 15 Å 21 Å

Solids of CdSe NQDs exhibit size dependent properties

Covalent linkages allow tailoring of electronic properties and directed energy transfer

New electronic materials are enabling new functionality



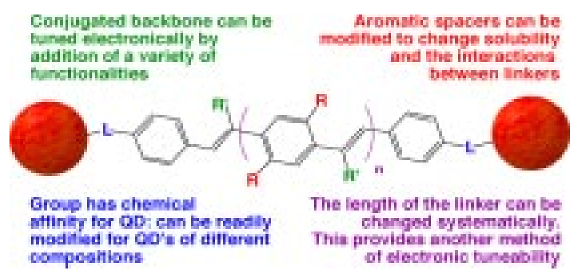
Nanometer Unit Cell

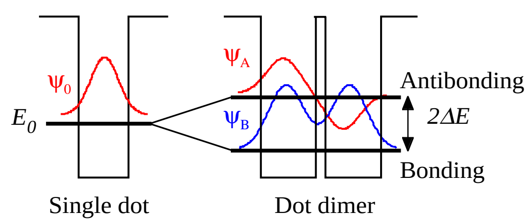
↓

C_{60} Curvature

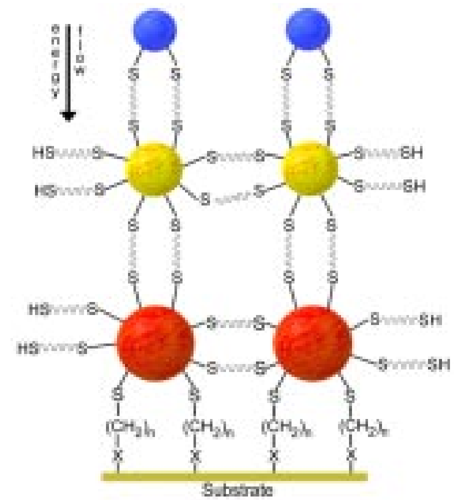
↓

Superconductivity



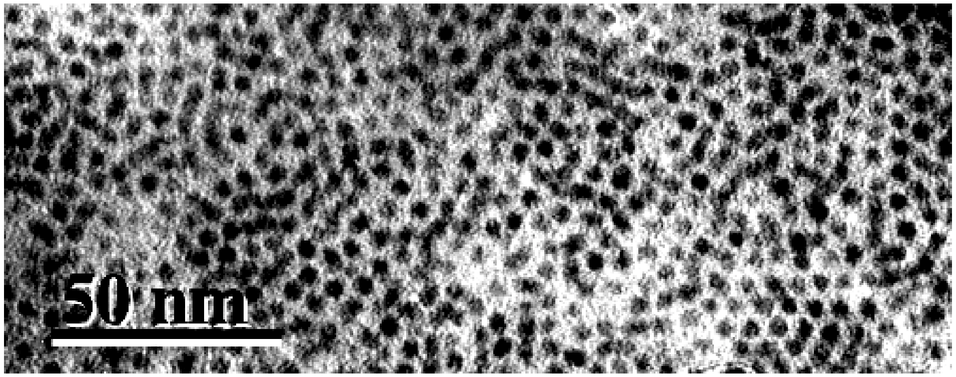


$E(dimer) = E_0 \pm \Delta E$



Gradient structure for directing energy flows

Quantum Dot Molecules and Solids Represent New Types of Artificial Solids



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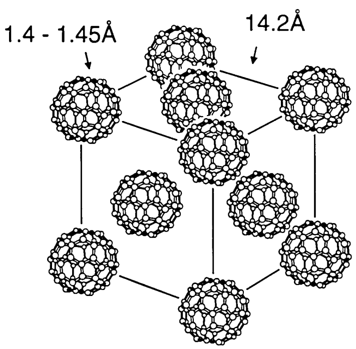
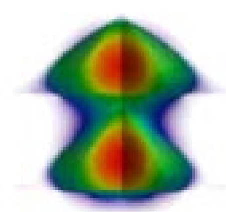
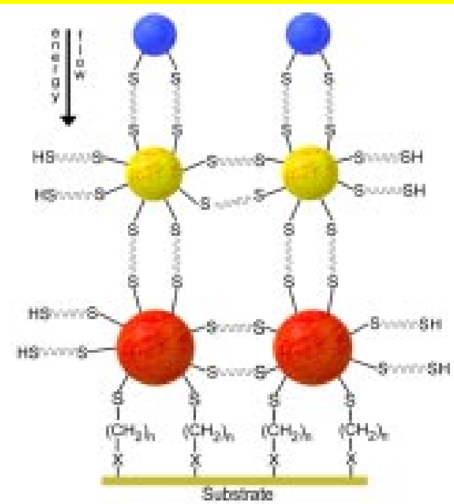


Nanometer Unit Cell
↓
C_{60} Curvature
↓
Superconductivity

Rabi flopping in stacked conical InAs QD dimers





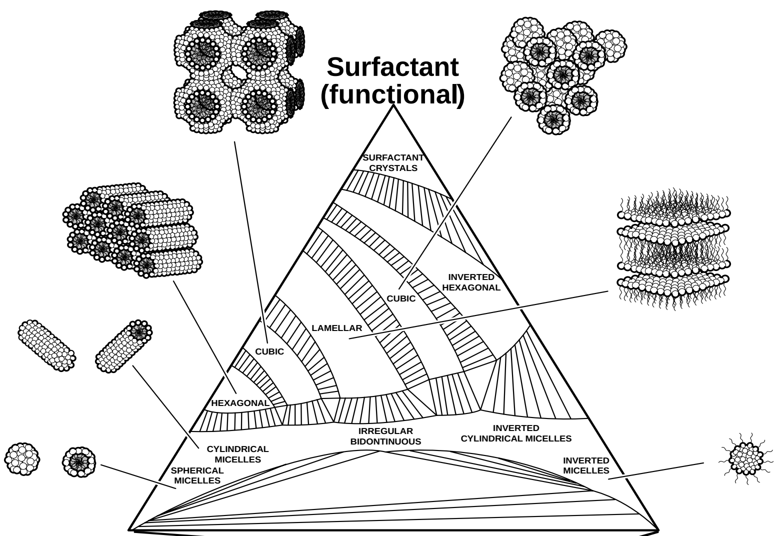
Gradient structure for directing energy flows

Malloy-University of New Mexico

Mesophases

Materials Self-Assembly Across Multiple Length Scales

Use polymerizable surfactants as structure-directing agents and monomers to create conjugated polymer nanocomposites



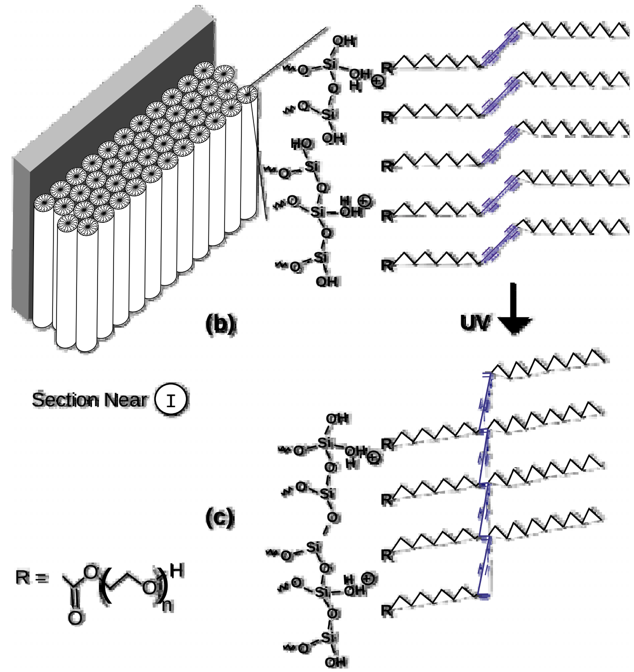
Water
Silicic acid & Other Hydrophilic Precursors

Ethanol Co-Solvent

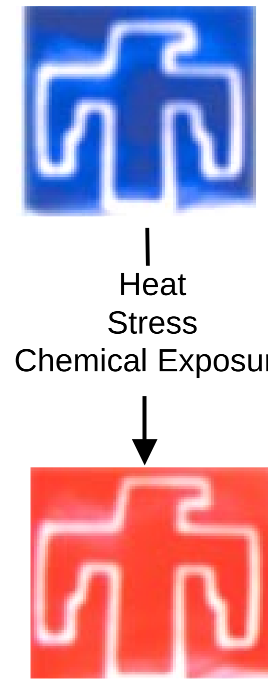
Oil
Monomers, Crosslinkers, Initiators & Other Hydrophobic Precursors

Detergent Phase Diagram

(Scriven, Davis)



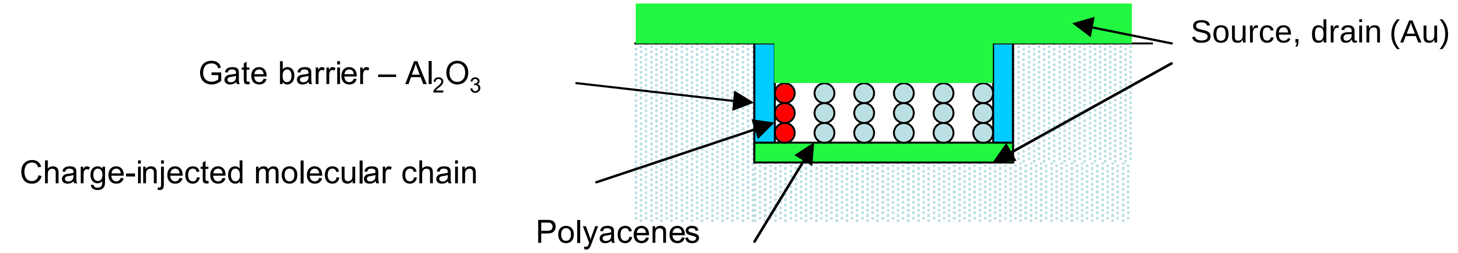
Self-assembly & topotactic polymerization
Nanostructure aligns, protects, and mediates performance



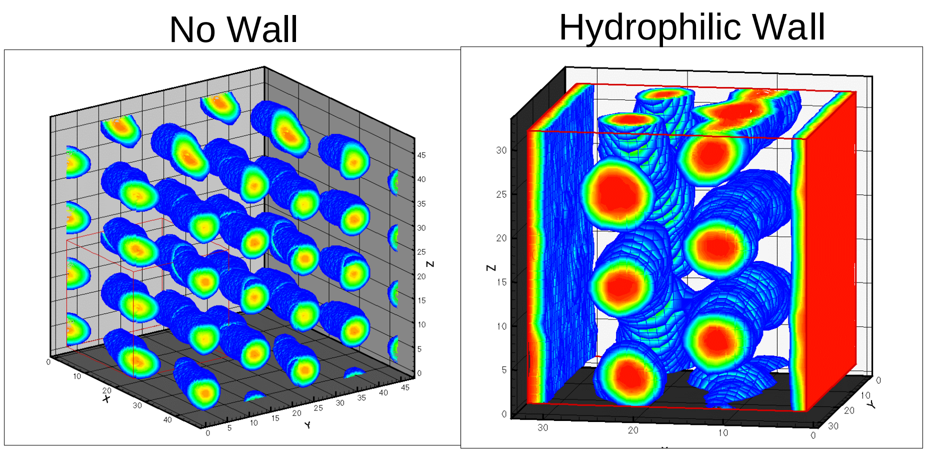
Emergent behavior
(Lu et al. ***Nature***, *2001)*

Nanostructuring of conjugated polymers may allow control of charge and energy transfer

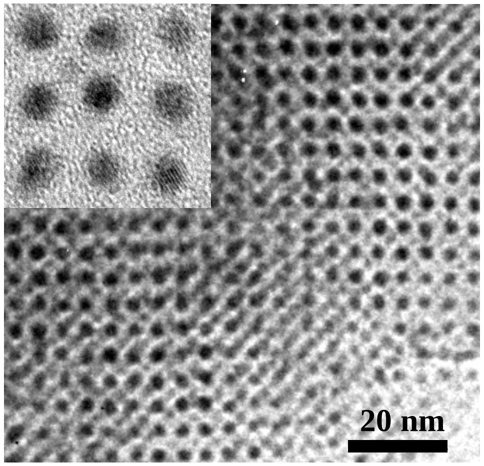
Nanomaterials Integration: Develop New Function, Understand and Exploit Effects of Interfaces, Dimensional Constraints, Collective Phenomena



Charge injection into organic single crystal allows single molecule switching



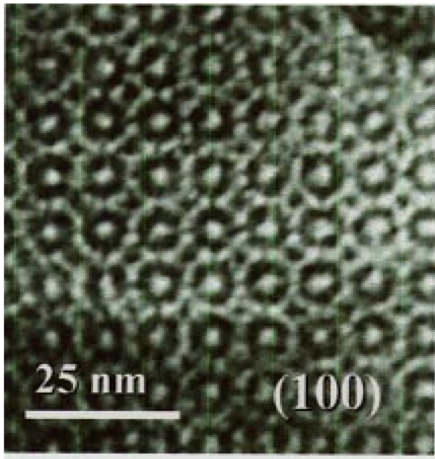
Orientation achieved through Interfacial interactions (van Swol)



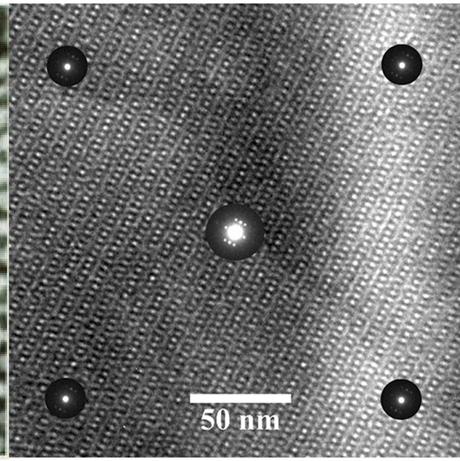
Self-assembly of QDs into robust inorganic nanostructure allows control of 3-D spatial arrangement (other than FCC), conducting to semi-conducting to insulating properties (Fan, Brinker, unpublished)

Evaporation-Induced Self-Assembly Enables Facile, Efficient Nano-Micro-Macro Integration

Membrane

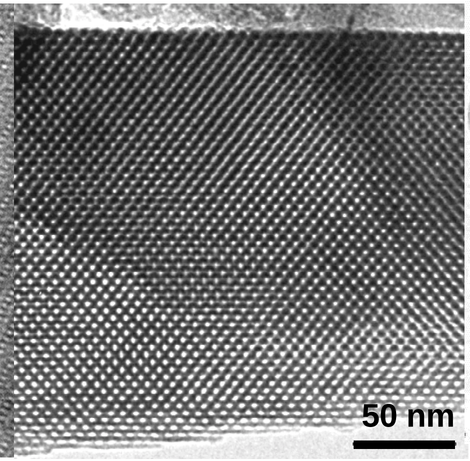


Sensor



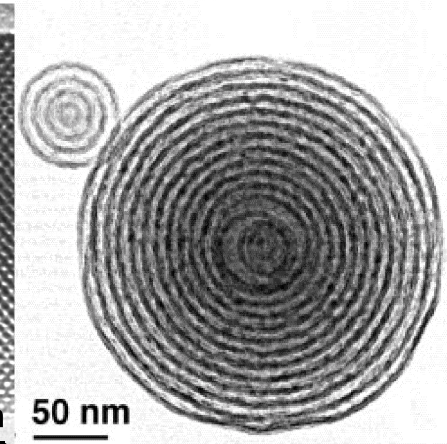
Lu et al., Nature 1997

low k



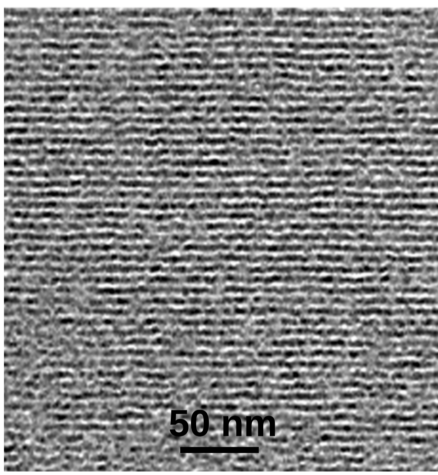
Brinker et al., Adv. Mater. 1999

Controlled release



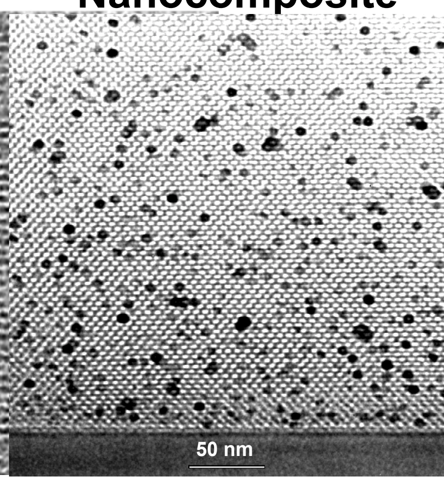
Lu, et al., Nature 1999

Sea-Shell



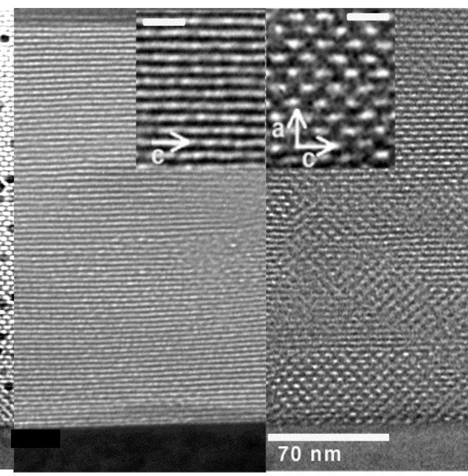
Sellinger et al., Nature 1998

Ag/Silica Nanocomposite



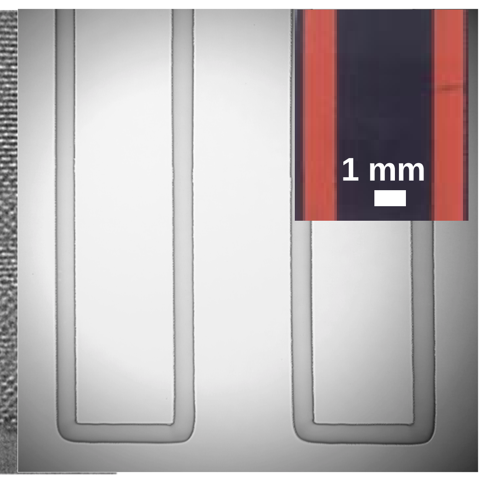
Fan et al., Unpublished

Phase Transition



Doshi et al., Science 2000

Patterns

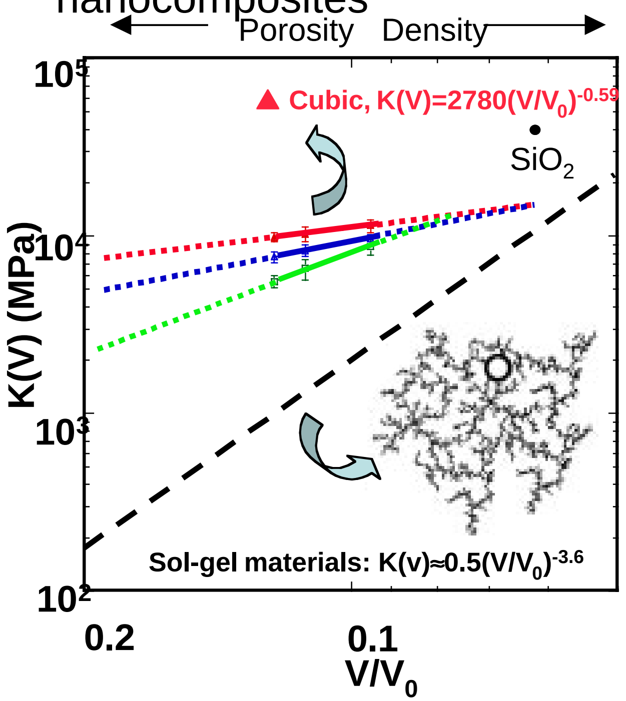


Fan et al., Nature 2000

The CINT Environment Will Foster Interactions With Other Thrust Areas and the Nanoscience Community

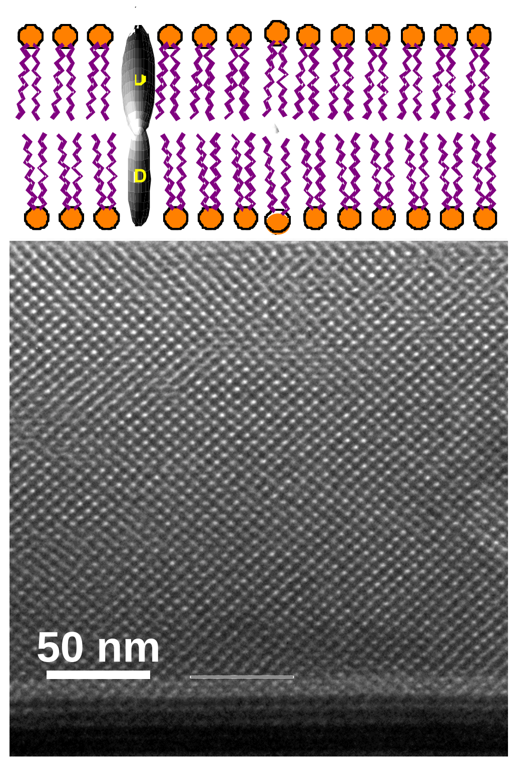
Nanomechanics (explore limits of continuum Mechanics)

- Investigate/model mechanical behavior of porous and composite nanostructures
- Study mechanochromism in conjugated polymer/inorganic nanocomposites



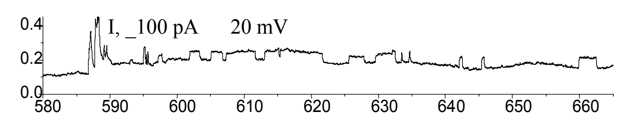
Nano-bio-micro interfaces (exploit porous architectures as water-filled solid state platforms)

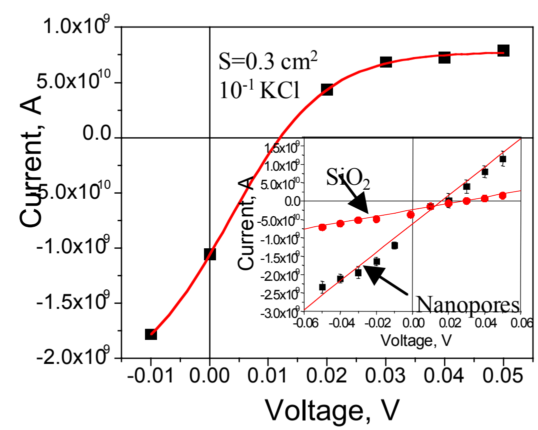
- New porous inorganic platforms for supported lipid bilayers and ion channels



Nanophotonics (exploit collective behavior)

- Large electro-optic responses
- Negative refractive index materials
- Dipolar nanocomposites
- Position QD arrays in photonic band gaps crystals

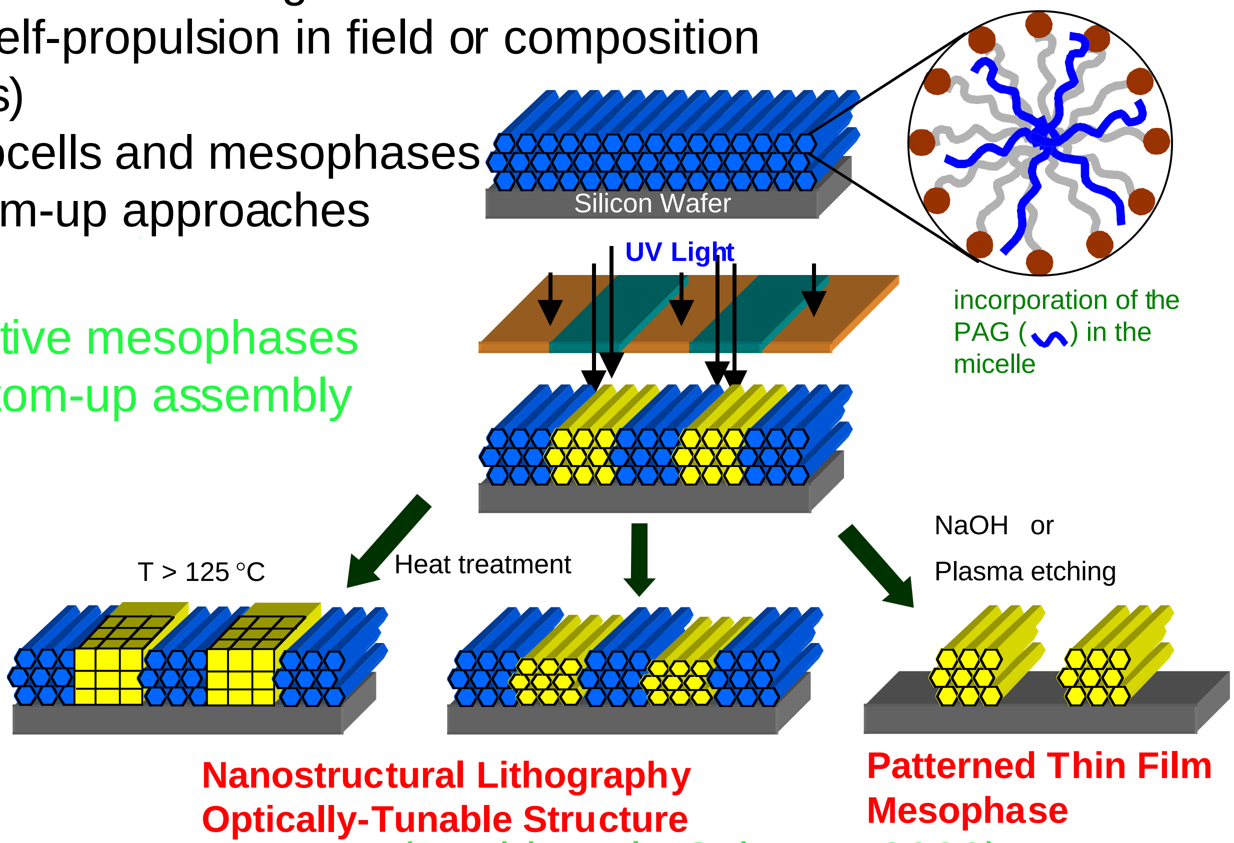




CINT Will Promote Discovery of New Materials and Functions

- Extend directed and self-assembly approaches by incorporation of nanocell complexes, quantum dots, and colloids; enhance interfacially-driven phenomena
- Explore complex material designs and/or synthesis procedures that employ or are derived from collective emergent behavior (Brownian ratchets, self-propulsion in field or composition gradients, chemotaxis)
- Serve as a “foundry” for nanocells and mesophases
- Combine top-down and bottom-up approaches

Self-assembly of photosensitive mesophases combines top-down and bottom-up assembly to achieve new functionality



(Doshi et al., Science, 2000)

Complex Functional Nanomaterials - Theory and Simulation

Issues / Challenges

Materials Design

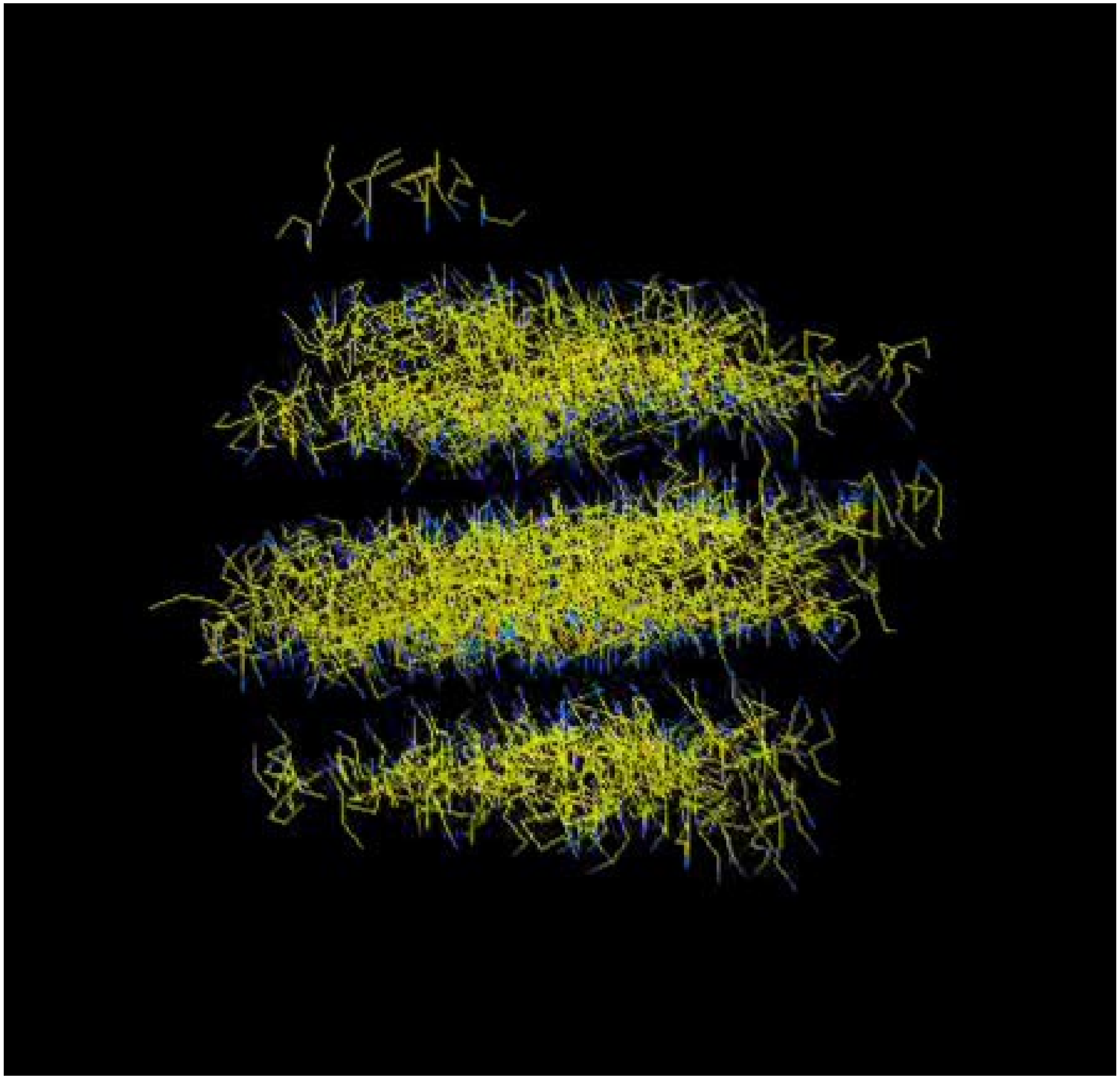
- Establish structure-property relationships of QDs (material type, size, spacing) and nanocomposites (materials, connectivity, interfacial phenomena) to design new artificial solids
- Understand effects of temperature, pressure, electric fields on synthetic molecular crystals to predict new emergent states and determine origins of microscopic parameters such as carrier density, Fermi velocity, and electron-phonon coupling

Nanofabrication

- Can we predict self-assembly of multiple materials into complex hierarchical designs?
- What is the influence of extended micro or macro-interfaces, and static or dynamic external fields?

Materials Performance

- Can we simulate optical, electronic, and transport behaviors of complex functional nanomaterials?



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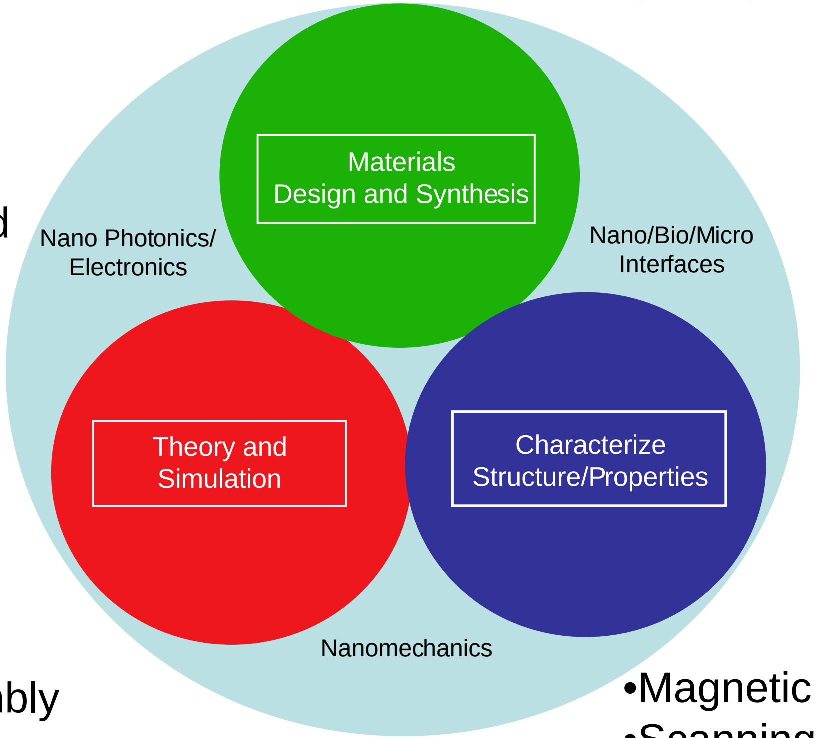
Interfaces with the Complex Functional Nanomaterials Thrust

SNL

- Self-assembled porous and composite nanostructures
  - -films
  - -particles
- QDs and arrays
- Magnetic field structured solids
- Micromachining / Advanced Lithography
- MBE

LANL

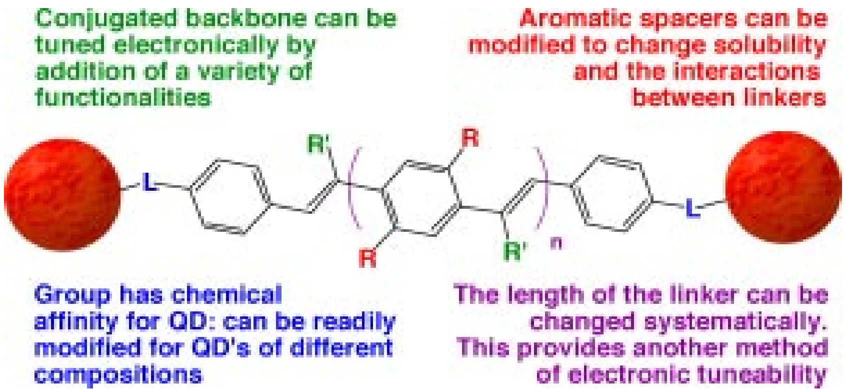
- Crystal growth facility
  - -complex nanocell oxides and organics
- QDs, QD molecules, QD solids



- Simulations of self-assembly
  - -surfactants
  - -colloidal crystallization
  - -directed assembly
  - -transport behavior
- Complexity / Collective behavior SNL, LANL, S.F. Institute

- Magnetic resonance force microscope
- Scanning probe and near field optical microscopies
- Atom tracker
- SANS
- SAXS
- Reflectometry

Interfaces with the Complex Functional Nanomaterials Thrust



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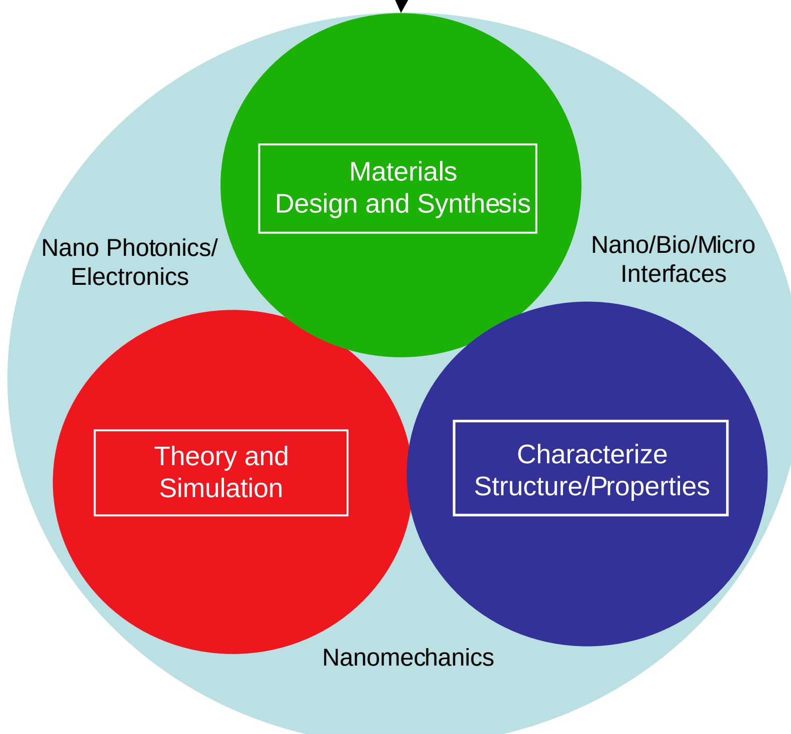

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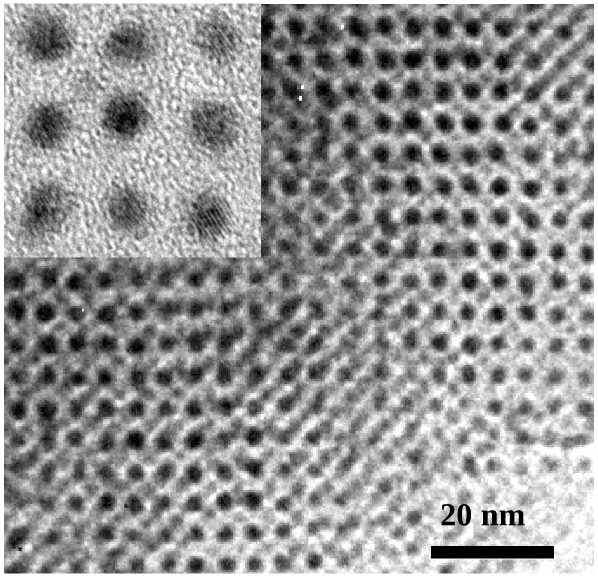

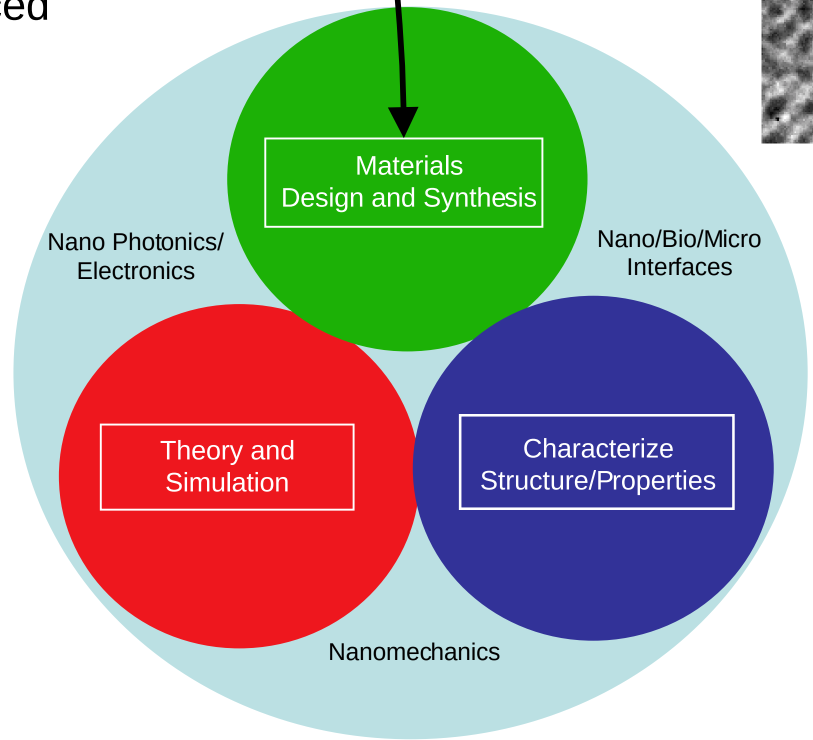

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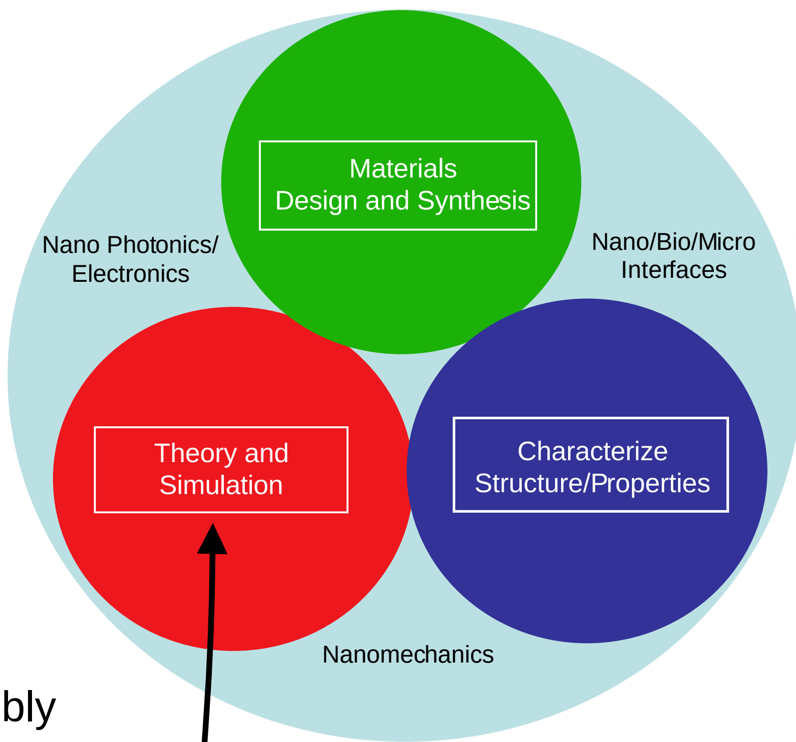

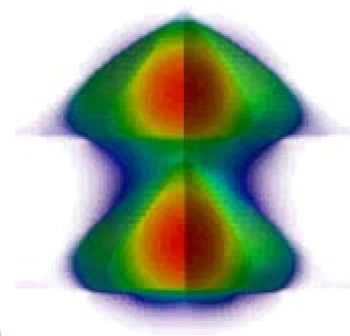

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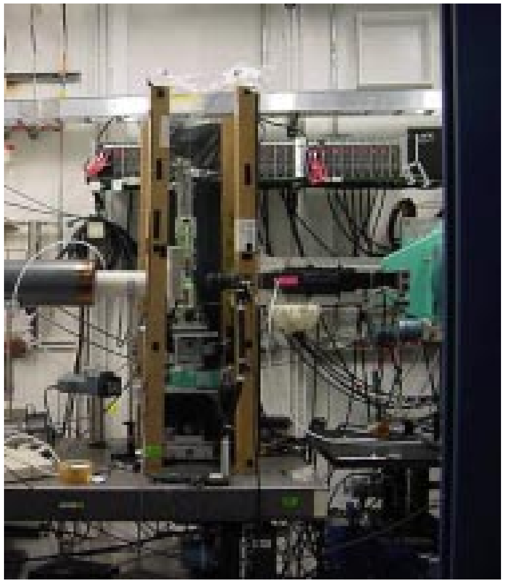
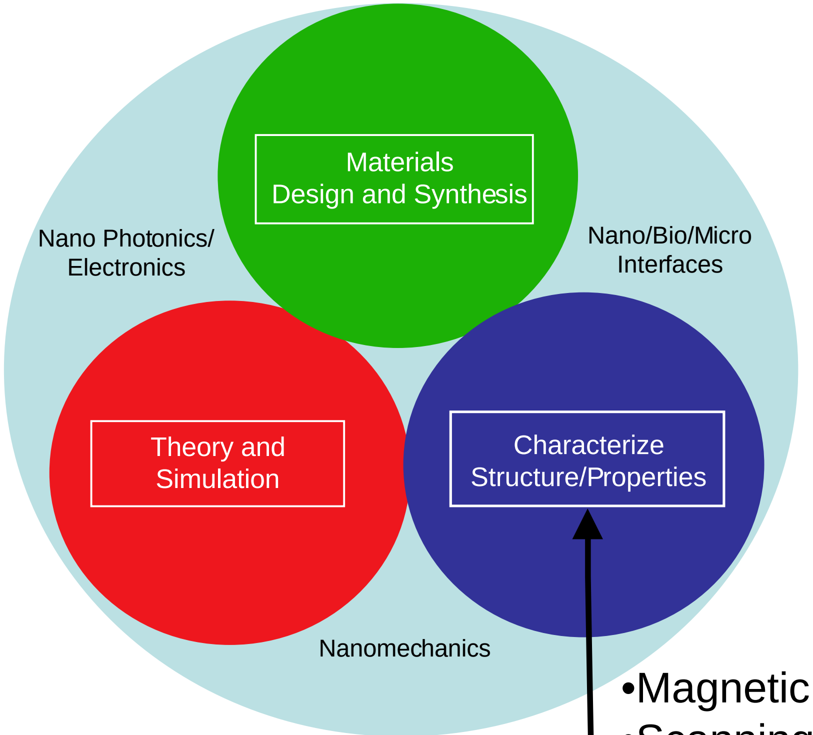


In situ grazing incidence SAXS of mesophase self-assembly at Argonne's Advanced Photon Source



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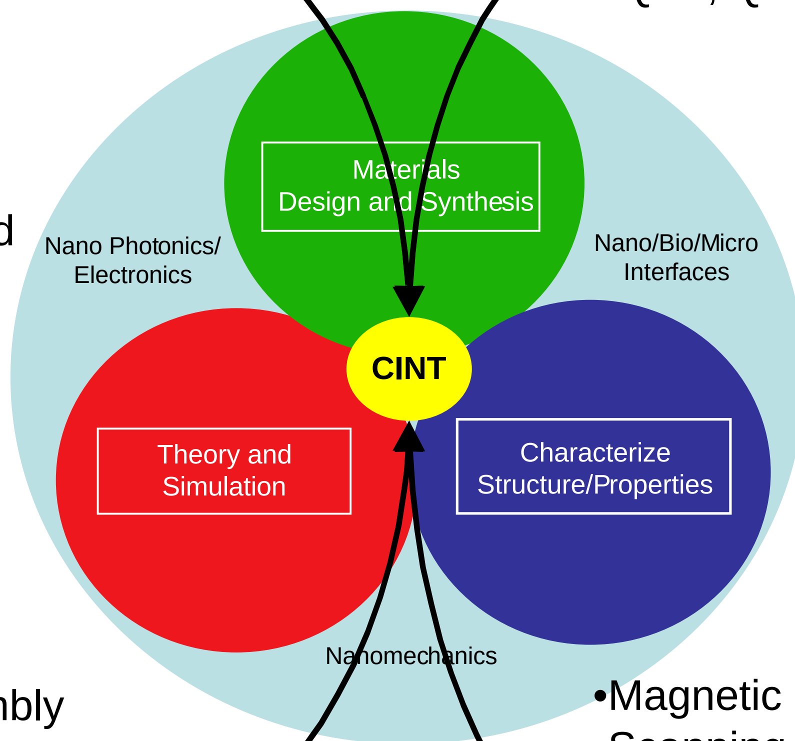

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